



RECEIVED

NOV 13 2003

TC 1700

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Mitsuhiro KUREISHI et al

Serial No.: 09/996,579

Filed: November 30, 2001

For: PHOTO MASK BLANK AND METHOD OF MANUFACTURING
THE SAME**TRANSLATOR'S DECLARATION**Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Sir:

I, Noriyasu Ikeda, of 1-15-7, Tamami, Asao-ku, Kawasaki-shi, Kanagawa, Japan, hereby certify that I am conversant with both the Japanese and the English languages, and that I have prepared the English translation attached hereto, which is a full, true and faithful translation of the patent application filed with the Patent Office of Japan under Application No. 367837/2000 on December 1, 2000 to the best of my knowledge and belief.

I further declare that all statements made in this declaration of my own knowledge are true and that all statements made on information and belief and believed to be true; and further, that these statements are made with the knowledge that willful, false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful, false statements may jeopardize the validity of this application or any Patent issued thereon.

October 30, 2003

Date



Name: Noriyasu Ikeda

(Translation)

Name of Document: Patent Application

Reference Number: P00HYE042

To: Commissioner, Patent Office

International Class: C03B 11/00

Inventor:

Address: c/o HOYA CORPORATION, 7-5, Naka-Ochiai
2-chome, Shinjuku-ku, Tokyo

Name: Mitsuhiro KUREISHI

Inventor:

Address: c/o HOYA CORPORATION, 7-5, Naka-Ochiai
2-chome, Shinjuku-ku, Tokyo

Name: Osamu NOZAWA

Applicant:

ID Number: 000113263

Address: 7-5, Naka-Ochiai 2-chome, Shinjuku-ku,
Tokyo

Name: HOYA CORPORATION

Representative: Hiroshi SUZUKI

Attorney:

ID Number: 100103676

Patent Attorney

Name: Yasuo FUJIMURA

Official Fee:

Deposit Number: 056018

Sum: 21,000 yen

List of Presented Documents:

Name: Specification 1

Name: Drawing 1

Name : Abstract 1



Registration Number of
Gen ral Power of Attorney: 9500007

Proof: Required

[Name of Document] Specification

[Title of the Invention] Photomask Blank and Method of
Manufacturing the Same

[Claims]

[Claim 1] A method of manufacturing a photomask blank by forming an opaque film or a semi-transmission film on a transparent substrate, said method comprising a step of:

forming said opaque film or said semi-transmission film onto the substrate by irradiating the substrate with ions generated by an ion generator separately disposed in a film formation chamber during the deposition of the opaque film or the semi-transmission film on the transparent substrate by a sputtering method.

[Claim 2] The method claimed in claim 1, wherein said step comprises:

controlling a film stress of the opaque film formed on the substrate; and

suppressing a warp amount of the substrate generated by the film formation to $\pm 0.1 \mu\text{m}$ or less, where (a warp amount of the substrate after film formation) - (a warp amount of the substrate before the film formation) = (a warp amount of the substrate generated by the film formation).

[Claim 3] The method claimed in claim 1 or 2, wherein said step comprises:

directly introducing an inert gas into the ion

generator from the outside of the film formation chamber;
and

ionizing said inert gas by the ion generator to
irradiate the substrate with the ions.

[Claim 4] The method claimed in claim 1 or 2,
wherein said step comprises:

directly introducing a reactive gas into the ion
generator from the outside of the film formation chamber;
and

ionizing said reactive gas by the ion generator and
irradiating the substrate with the ions.

[Claim 5] A photomask blank prepared by the method
according to any one of claims 1 to 4.

[Claim 6] A photomask prepared by using the
photomask blank according to claim 5.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a photomask for use
in manufacturing a semiconductor integrated circuit and the
like, a photomask blank as a material of the photomask, and
a method of manufacturing the photomask blank.

[0002]

[Description of Prior Art]

In manufacturing semiconductors such as a
semiconductor element, IC, and LSI, a manufacturing process
of a photomask for use in transferring a fine pattern onto

a semiconductor wafer usually includes: a film forming step of forming films, such as an opaque film, a semi-transmission film (a translucent film), onto a transparent substrate obtained by precisely polishing synthetic quartz glass by sputtering and the like; a resist coating step of coating a resist film on the films, such as the opaque film, by a spin coating method; an exposure step (delineating step) of irradiating a resist surface with an electron ray or a laser beam to selectively expose the resist film; a development step of developing the exposed resist film with a predetermined developer to form a resist pattern; an etching step of using the resist pattern as a mask to etch the films such as the opaque film and to obtain a predetermined opaque film pattern, and the like. In this case, the substrate thus obtained by the film forming step is generally called a photomask blank.

Here, in the forming step of forming the opaque film, usually from a viewpoint of productivity, the film is formed by a usual DC magnetron sputtering method by using a DC magnetron sputtering apparatus and a chromium target. Alternatively, a thin film is formed by a reactive sputtering method executed by introducing at least one of gases such as nitrogen and oxygen.

[0003]

Chromium or a chromium compound is used as the opaque film in an original sheet of the photomask, that is, a binary photomask blank, in which light intensity modulation

is used to transfer the pattern. In addition, the sputtering method is mainly utilized as a method for forming the opaque film onto the substrate. However, when the opaque film such as a chromium film is formed by the sputtering method, the opaque film usually has a tensile stress, and the photomask blank including the transparent substrate as a base therefore warps. Such warps bring about a high possibility of an insufficient focus depth for exposure or a design defect. This results in deterioration of the photomask blank. Here, for a warp amount of the substrate, the substrate is measured by flatness measuring instrument by an optical interferometer, such as FM200 manufactured by TROPEL Co. In this case, a difference of height (P-V value) between a highest point and a lowest point from a level surface of the substrate is measured before and after the film formation, and the warp amount of the substrate generated by the film formation is defined by the difference of the P-V value before and after the film formation. That is, definition is made by:

$$\begin{aligned} & (\text{warp amount of substrate after film formation}) \\ & - (\text{warp amount of substrate before film formation}) \\ & = (\text{warp amount of substrate generated by film} \\ & \text{formation}). \end{aligned}$$

As a stress reduction method of the opaque film, there is a method of applying a bias to a substrate side during sputtering deposition and implanting ions present in plasma. However, since the photomask blank has a relatively large

film formation area, and the substrate is a dielectric such as glass, it is difficult to obtain a uniform effect within the surface.

[0004]

On the other hand, when a chromium compound thin film is formed as the opaque film, or a compound thin film such as MoSiN, MoSiON, SiON, SiN is formed as a semi-transmission film (phase shifter film), the film is usually formed by the reactive sputtering method such as the DC magnetron sputtering. During the film formation, however, the compound is also deposited on the surface of a target, and electric discharge becomes unstable (as a result, particles are generated by abnormal discharge). Therefore, there is a problem that a defect is liable to occur in the photomask blank. Furthermore, the reactive sputtering method has a lower deposition rate and therefore has a problem of low productivity, as compared with the usual non-reactive DC magnetron sputtering method. When the compound target is used to form the film by an RF magnetron sputtering method instead of the DC magnetron sputtering method, plasma during the film formation is widely spread as compared with the DC magnetron sputtering method. Therefore, the film is undesirably deposited inside a chamber, and acts as a generation source of particles on the mask blank and, as a result, there arises a problem that the defect is liable to occur in the photomask blank.

[0005]

Moreover, in consideration of precision of a size recently required for the mask pattern, it has been necessary to thin a resist and opaque film during pattern formation. However, in a thin film forming method using the conventional DC magnetron sputtering method, the chromium film is inferior to a bulk film in density and denseness. As a result, a sufficient optical density is not fully obtained, and therefore a demand for thin film formation cannot be satisfied.

[0006]

[Problem to be Solved by the Invention]

The present invention has been provided to solve the aforementioned problems, and a first object thereof is to reduce a warp of a substrate caused by a film stress in a photomask blank (to relax and control the film stress).

Moreover, a second object of the present invention is to thin a film by enhancement of density and denseness, particularly to thin an opaque film by enhancement of a shielding property, and to enhance resistance to chemicals and resistance to light by enhancement of denseness.

Furthermore, a third object of the present invention is to reduce film defects by a reduction of particles by abnormal discharge in a reactive DC sputtering method or by a reduction of the particles in a reactive RF sputtering method during formation of a compound opaque film or a compound semi-transmission film by a reactive sputtering method, and to enhance a deposition rate (enhance

productivity) by acceleration of reactivity (promotion of reactivity).

Additionally, a fourth object of the present invention is to provide a high-quality photomask blank and photomask prepared in consideration of the aforementioned objects.

[0007]

[Means to Solve the Problem]

To achieve the aforementioned objects, the present invention has the following features.

(Feature 1) A method of manufacturing a photomask blank for forming an opaque film or a semi-transmission film on a transparent substrate, the method comprising a step of forming the opaque film or the semi-transmission film onto the substrate by irradiating the substrate with ions generated by an ion generator separately disposed in a film formation chamber during the deposition of the opaque film or the semi-transmission film on the transparent substrate by a sputtering method.

[0008]

(Feature 2) The method of manufacturing the photomask blank according to Feature 1, wherein the step comprises controlling a film stress of the opaque film formed on the substrate; and suppressing a warp amount of the substrate generated by the film formation to $\pm 0.1 \mu\text{m}$ or less, where (a warp amount of the substrate after film formation) - (a warp amount of the substrate before the

film formation) = (a warp amount of the substrate generated by the film formation).

[0009]

(Feature 3) The method of manufacturing the photomask blank according to Feature 1 or 2, wherein the step comprises directly introducing an inert gas into the ion generator from the outside of the film formation chamber; and ionizing the inert gas by the ion generator and irradiating the substrate with the ions.

[0010]

(Feature 4) The method of manufacturing the photomask blank according to Feature 1 or 2, wherein the step comprises directly introducing a reactive gas into the ion generator from the outside of the film formation chamber; and ionizing the reactive gas by the ion generator and irradiating the substrate with the ions.

[0011]

(Feature 5) A photomask blank prepared by the method according to any one of Features 1 to 4.

[0012]

(Feature 6) A photomask prepared by using the photomask blank according to Feature 5.

[0013]

[Operations of the Invention]

According to Feature 1, the opaque film or the semi-transmission film is formed onto the substrate by the sputtering method, and the substrate is irradiated with

ions generated by the ion generator (hereinafter referred to as an ion source) separately disposed in the film formation chamber (a film material being deposited on the substrate is irradiated), by which density and denseness of a thin film can be enhanced. Thereby, the opaque film achieves an effect that the opaque film is thinned by enhancing a shielding property by the enhancement of density and denseness and that chemical durability is enhanced by the enhancement of denseness. Moreover, the semi-transmission film (phase shifter film) achieves an effect that the semi-transmission film is thinned by the enhancement of density and denseness, and the chemical durability, irradiation durability, and the like are enhanced by the enhancement of denseness. In this case, along with an increase of irradiation energy of ions emitted from the ion source, the density and denseness can be enhanced.

Moreover, according to Feature 1, the substrate is directly irradiated with ions from the ion source during sputtering deposition, thereby enabling a control of a film stress. This makes it possible to relax or control the stress of the opaque film therefor. Concretely, for example, a Cr film formed by sputtering without ion irradiation has a tensile stress. According to the present invention, however, the substrate is directly irradiated with ions from the ion source during the sputtering deposition and the irradiation energy is controlled, by

which the tensile stress can be reduced, also be controlled to be zero, or further controlled to be on a compressive stress side. Moreover, for the semi-transmission film (phase shifter film), it is possible to control the stress of the semi-transmission film.

When heat treatment is not performed as described later, the irradiation energy is preferably controlled in consideration of the reduction effect of stress and the enhancement effect of density.

Furthermore, according to Feature 1, in a film formation process of the compound opaque film or the compound semi-transmission film by the reactive sputtering method, the substrate is directly irradiated with ions from the ion source during the sputtering deposition. Thereby, reaction is accelerated (promoted) in the vicinity of the substrate and efficiently carried out. Therefore, its deposition rate is high and productivity is enhanced as compared with a conventional reactive sputtering method in which the substrate is not irradiated with ions from the ion source.

In the present invention, a preferable type of the ion source may irradiate ions of a high current density and low energy for the purpose of improving a film quality, and, specifically, may be, for example, an RF type, end hall type, Kaufmann type, and ECR type, but this invention is not limited to the above-mentioned types of ion sources.

[0014]

According to Feature 2, the method of Feature 1 is used to control the stress of the opaque film formed on the substrate, and it is possible to suppress the warp amount of the substrate generated by the film formation to $\pm 0.1 \mu\text{m}$ or less, assuming that (the warp amount of the substrate after the film formation) - (the warp amount of the substrate before the film formation) = (the warp amount of the substrate generated by the film formation).

[0015]

In Feature 2, the method of Feature 1 is used to control the stress of the opaque film or the semi-transmission film formed on the substrate. Furthermore, the stress of the opaque film or the semi-transmission film is controlled by applying thermal treatment or laser irradiation treatment. Thereby, it is possible to suppress a change amount from a warp state measured before the film formation to $\pm 0.1 \mu\text{m}$ or less, assuming that (the warp amount of the substrate after the thermal treatment or the laser irradiation treatment) - (the warp amount of the substrate before the film formation) = (the change amount from the warp state measured before the film formation).

Concretely, for example, with a change of the irradiation energy of the ion source, the stress of the opaque film is controlled to be on the compressive stress side. Thereafter, being subjected to the thermal treatment or the laser irradiation treatment, the stress of the opaque film is reduced and controlled to be in the vicinity

of zero. Additionally, the ion irradiation energy can be controlled with a control of a beam acceleration voltage and anode current. Moreover, for example, when the stress of the semi-transmission film is a compressive stress, the film is subjected to the thermal treatment or the laser irradiation treatment, by which the stress of the semi-transmission film can be reduced or controlled to be in the vicinity of zero. In this case, it is unnecessary to control the irradiation energy of the ion source in view of the stress reduction effect as described above. It is then possible to aim only at the enhancement of the density, when the irradiation energy of the ion source is controlled. Therefore, the density can further be enhanced.

Additionally, a thermal treatment temperature is preferably 150°C or more, 200°C or more, 250°C or more, 300°C or more, 350°C or more, 380°C or more, or 550°C or more. In this case, when the thermal treatment temperature is higher, an internal stress can be reduced, but a change amount of transmittance also increases. Additionally, when the temperature is excessively raised, a time of temperature rise or drop is lengthened. This causes a problem of deteriorated productivity. Therefore, the thermal treatment temperature is preferably 700°C or less. A thermal treatment time may be, for example, one minute or more as long as heat is conducted through the entire semi-transmission film within this time.

An atmosphere for the thermal treatment preferably

includes no reactive atmosphere such as oxygen. If the reactive atmosphere is included, a composition in a film thickness direction changes with the thermal treatment. Therefore, a preferable atmosphere includes an inert gas such as nitrogen or argon.

The thermal treatment may be performed after the semi-transmission film is formed on the transparent substrate (in a blank state) or after the semi-transmission film is patterned (in a mask state). Note that, however, when a fine pattern is thermally treated at a high temperature, a pattern shape is possibly deteriorated. The thermal treatment performed in the blank state has an effect that a film quality fluctuation in the subsequent baking process of the resist (200°C or less, e.g., about 180°C) is suppressed. In order to achieve the effect, the film is preferably thermally treated at a temperature higher than the baking temperature of the resist (e.g., 200°C or more).

[0016]

According to Feature 3, the inert gas is directly introduced into the ion generator from the outside of the film formation chamber and ionized by the ion generator, and the substrate is irradiated with the ions. Thereby, the inert gas ions can efficiently be supplied to the substrate as compared with introduction of the inert gas only via a sputtering gas introducing port. Therefore, the aforementioned reduction effect of the film stress and the

enhancement effect of the film density can further be increased.

[0017]

According to Feature 4, the reactive gas is directly introduced into the ion generator from the outside of the film formation chamber and ionized by the ion generator, and the substrate is irradiated with the ions. Thereby, the reactive gas ions can efficiently be supplied to the substrate as compared with the introduction of the reactive gas only via the sputtering gas introducing port. Therefore, it is possible to further increase a reaction speed, to increase the aforementioned reduction effect of the film stress and the enhancement effect of the film density, and to achieve satisfactory controllability of the film. Moreover, when the reactive gas is introduced only via a gas introducing port for the ion source, an amount of the reactive gas to be introduced into the film formation chamber can be reduced as compared with the introduction of the reactive gas only via the sputtering gas introducing port. As a result, since generation of the compound on the target can be inhibited, abnormal discharge in the reactive DC sputtering method can be reduced. Moreover, since the film is inhibited from being deposited inside the chamber, the particles in the reactive RF sputtering method can be reduced, thereby enabling a reduction of the film defects.

[0018]

According to Features 5 and 6, there can be provided

a high-quality photomask blank and photomask prepared in consideration of various factors such as, for example, the reduction of warp of the substrate, thinning of the film by the enhancement of density and denseness, enhancement of chemical durability and irradiation durability by the enhancement of denseness, and reduction of film defects during preparation of the compound opaque film or the compound semi-transmission film by the reactive sputtering method.

[0019]

[Examples]

Example 1

Examples of the present invention will be described hereinafter in detail with reference to the drawing.

In an apparatus shown in Fig. 1, an ion source 11 is arranged in a vacuum chamber 1 of a general DC magnetron sputtering apparatus. In the chamber 1, disposed are a magnetron cathode 3 with a chromium target 5 having a size of $\phi 6$ inches and a thickness of 5 mm disposed thereon, a synthetic quartz substrate 6 having a size of six inches square and a thickness of 0.25 inch, and an ion source 11 of an end hall type. The ion source 11 is disposed at an appropriate angle so as to emit ions toward the substrate 6. In this case, a length of a straight line from a target center to a substrate surface center is 23 cm, and a length of a straight line from the ion source to the substrate surface center is 16 cm. Moreover, the chamber was

evacuated to a degree of vacuum of 1×10^{-4} Pa by an exhaust pump.

Subsequently, an argon gas was introduced via a sputtering gas introducing port 7 and a gas introducing port 12 for the ion source so as to have a pressure of 0.11 Pa inside the chamber. Power of 300 W was applied to the cathode 3 using a sputtering DC power source 9. Simultaneously with it, the substrate 6 was irradiated with argon ions using the ion source 11 on conditions that a beam acceleration voltage was 60 V and an anode current was 0.8 A (controlled by an anode and cathode power source controller 13 for the ion source), and an opaque film was formed or deposited to a film thickness of 80 nm.

Checking a warp state of the substrate using an optical interferometer, we found that a change amount of 0.1 μm was given from the warp state measured before film formation ((a warp amount of the substrate after the film formation) - (the warp amount of the substrate before the film formation) = (the warp amount of the substrate generated by the film formation)). In this event, a film stress was a tensile stress. Furthermore, the film was formed on similar conditions, only by changing irradiation conditions such as the beam acceleration voltage of 80 V and the anode current of 1A. As a result, the warp amount of the substrate generated by the film formation was 0.1 μm , and the film stress was a compressive stress. That is, by controlling the irradiation conditions of the ion source,

the film stress can be adjusted to a compressive stress side from a tensile stress side, and the resultant film stress can be adjusted to be zero or in the vicinity of zero.

[0020]

Comparative Example 1

For comparison with Example 1, with an arrangement of an apparatus not including the ion source of Example 1, evacuation was made to a degree of vacuum of 1×10^{-4} Pa, an argon gas was introduced to attain a pressure of 0.11 Pa, and power of 300 W was supplied from the sputtering DC power source 9 to the cathode 3, so that a film was deposited to a film thickness of 80 nm.

The warp amount of the substrate generated by the film formation or deposition was measured like in Example 1 and found to be 0.5 μm . In this event, the film stress was the tensile stress.

It is understood from Example 1 and Comparative Example 1 that according to the present invention it is possible to improve flatness of a mask blank as compared with the conventional method.

[0021]

Example 2

With an arrangement of the apparatus similar to that of Example 1, power of 600 W was supplied from the sputtering DC power source 9 to the cathode 3 and, simultaneously with it, ions were emitted from the ion

source 11 toward the substrate 6 on conditions that a beam acceleration voltage was 80 V and anode current was 1A, in order to form a film having an optical density (O.D.) of 3 for a wavelength 193 nm. Thus, a film thickness of 41 nm was achieved. Moreover, the film was deposited to a film thickness of 1 μm on the aforementioned film formation conditions and, thereafter, measurement was made about weights of the substrate before and after the film formation. Density of the chromium film was calculated. As a result of the calculation, the density of the chromium film was 7.1 g/cm³.

Additionally, with the chromium film, the film density preferably falls in a range of 95 to 100%, particularly preferably 98% or more of a bulk density (7.2 g/cm³).

[0022]

Comparative Example 2

For comparison with Example 2, with an arrangement of an apparatus not including the ion source of Example 1, evacuation was made to a degree of vacuum of 1×10^{-4} Pa, an argon gas was introduced to attain a pressure of 0.11 Pa, power of 600 W was supplied from the sputtering DC power source 9 to the cathode 3, and the film was formed so as to have the optical density (O.D.) of 3 for the wavelength of 193 nm. The resultant film thickness was 45 nm. Moreover, the film was deposited to a film thickness of 1 μm on the aforementioned film formation conditions, and the density

of the film was calculated from the weights of the substrate before and after the film formation. As a result, the film density was 6.7 g/cm³.

[0023]

Example 3

The chromium film was formed to a thickness of 65 nm on the synthetic quartz substrate 6 having a size of six inches and a thickness of 0.25 inch with an arrangement of an apparatus and film formation conditions similar to those of Example 1. Subsequently, 50 sccm of the argon gas was introduced onto the chromium film via the sputtering gas introducing port 7, and power of 300 W is supplied from the sputtering DC power source 9 to the cathode 3 to cause a sputtering discharge. Moreover, during the sputtering discharge, a mixture gas containing 4 sccm of a nitrogen gas and 0.5 sccm of an oxygen gas was introduced via the gas introducing port 12 for the ion source. The substrate 6 was then irradiated with nitrogen ions and oxygen ions from the ion source 11 on conditions that the acceleration voltage was 160 V and the anode current was 1A, and an anti-reflection film was formed to a thickness of 28 nm.

The DC magnetron sputtering discharge was observed and no abnormal discharge was found.

[0024]

Comparative Example 3

For comparison with Example 3, with an arrangement of an apparatus not including the ion source of Example 1, the

chromium film was deposited to a thickness of 65 nm, and a film having an anti-reflection effect equivalent to that of Example 3 was formed as an anti-reflection layer by the DC magnetron sputtering method without ion irradiation. Thereby, the following flow rates were obtained: 38.4 sccm for the argon gas; 10 sccm for the nitrogen gas; and 1.6 sccm for the oxygen gas. Furthermore, the abnormal discharge was observed in the vicinity of the target during discharge. As a result, particles adhered onto the substrate with the film deposited thereon. Thus, it was impossible to form a high-quality photomask blank.

It is understood from Example 3 and Comparative Example 3 that an amount of the reactive gas to be introduced into the film formation chamber only via the gas introducing port for the ion source can be reduced as compared with the introduction of the reactive gas only via the sputtering gas introducing port. As a result, since generation of a compound on the target can be suppressed, the abnormal discharge in the reactive DC sputtering method can be reduced. This shows that film defects can be reduced.

[0025]

Example 4

With an arrangement of an apparatus similar to that of Example 1 and in which a silicon target was disposed as the target 5, 20 sccm of the argon gas via the sputtering gas introducing port 7 and 5 sccm of the nitrogen gas via

the gas introducing port 12 for the ion source were introduced onto the synthetic quartz substrate 6 having a size of six inches and a thickness of 0.25 inch, so that the chamber 1 attains the gas pressure of 0.1 Pa. Power of 200 W was then applied to the cathode 3, the sputtering discharge was thus caused to occur, and the substrate 6 was irradiated with the nitrogen ions from the ion source 11 on conditions that the acceleration voltage was 100 V and anode current was 1.1 A during the sputtering discharge. A thickness of an SiN film was then adjusted in order to obtain a phase angle of 180 degrees for a wavelength of 193 nm in forming a film. The formed SiN film was measured with a spectrophotometer and found to have a transmittance of 4.9% for the wavelength of 193 nm. In this connection, a transmittance of a semi-transmission film is preferably in a range of 3% to 20%.

[0026]

Comparative Example 4

For comparison with Example 4, with an arrangement of an apparatus in which the ion source of Example 1 was not used and in which a silicon target was disposed instead of the chromium target, 20 sccm of the argon gas and 5 sccm of the nitrogen gas were introduced via the sputtering gas introducing port 7, and power of 200 W was supplied from the sputtering DC power source 9 to the cathode 3. Like in Example 4, the film thickness was then adjusted in order to obtain the phase angle of 180 degrees in forming a film.

The transmittance for the wavelength of 193 nm was measured with a spectrophotometer and found to be 0.1%. Therefore, the transmittance was inappropriately outside the range of 3% to 20%.

It is understood from Example 4 and Comparative Example 4 that in the introduction of the reactive gas only via the gas introducing port for the ion source, the reactive gas ions can efficiently be supplied to the substrate as compared with the introduction of the reactive gas only via the sputtering gas introducing port. As a result, it is understood that the transmittance of the semi-transmission film can be improved by the enhancement of density and denseness.

[0027]

Example 5

With an arrangement of an apparatus similar to that of Example 4, 10 sccm of the argon gas via the sputtering gas introducing port 7 and 5 sccm of the nitrogen gas via the gas introducing port 12 for the ion source were introduced onto the synthetic quartz substrate 6 having a size of six inches and a thickness of 0.25 inch in the chamber 1, so that the chamber 1 attains a gas pressure of 0.11 Pa. Power of 600 W was then supplied from the DC power source 9 to the cathode 3, the sputtering discharge was thus caused to occur, and the substrate 6 was irradiated with the nitrogen ions from the ion source 11 on conditions that the acceleration voltage was 150 V and

anode current was 1.1 A during the sputtering discharge. The thickness of the SiN film was then adjusted in order to obtain a phase angle of 180 degrees for 193 nm in forming a film.

The transmittance and reflectance of the formed SiN film were measured with a spectrophotometer and a refractive index n and an extinction coefficient k for the wavelength of 193 nm were calculated from these experimental results. It was then found that $n = 2.6$, $k = 0.46$. Furthermore, in this case, the film deposition rate was checked, and was found to be 60 nm/min.

[0028]

Comparative Example 5

For comparison with Example 5, with an arrangement of an apparatus not including the ion source of Example 4, a nitrogen flow rate was adjusted, so that 10 sccm of the argon gas and 10 sccm of the nitrogen gas were introduced via the sputtering gas introducing port 7 in order to obtain the same phase angle and transmittance as those of Example 5. Power of 200 W was supplied from the DC power source 9 to the cathode 3, and an SiN film having the same phase angle and transmittance as those of Example 5 was formed.

The film deposition rate was then checked and found to be 20 nm/min.

It is understood from Example 5 and Comparative Example 5 that, in the introduction of the reactive gas

only via the gas introducing port for the ion source, the reactive gas ions can efficiently be supplied to the substrate as compared with the introduction of the reactive gas only via the sputtering gas introducing port, thereby increasing the film deposition rate and productivity.

Moreover, the semi-transmission film obtained in Example 5 was superior to the semi-transmission film obtained in Comparative Example 2 in denseness, chemical durability, and irradiation durability.

Furthermore, when the semi-transmission film obtained in Example 5 was thermally treated, it was possible to remarkably reduce the compressive stress of the film as compared with the semi-transmission film obtained in Comparative Example 2.

[0029]

While the preferred examples of the present invention have been described, the present invention is not limited to the aforementioned examples.

For example, the target may be disposed opposite to the substrate right under the substrate. Moreover, a plurality of targets may be offset from right under the substrate, and arranged in the film formation chamber. Further, the substrate can rotate itself.

The ion source may be disposed in any position in which the substrate can be irradiated with ions.

Even with use of an apparatus in which RF sputtering is performed instead of DC sputtering, the ion source may

be disposed, and the similar effect can be obtained.

[0030]

[Effects of the Invention]

According to the present invention, it is possible to reduce the warp of the substrate by the film stress generated in the photomask blank (to relax and control the film stress). Moreover, it is possible to thin the film by the enhancement of density and denseness, particularly to thin the opaque film by enhancement of a shielding property, and to enhance chemical durability, irradiation durability, and the like by the enhancement of denseness. Furthermore, it is possible to reduce film defects by a reduction of abnormal discharge and by a reduction of particles in forming the compound opaque film or the compound semi-transmission film by the reactive sputtering method, and to enhance the deposition rate (enhance the productivity) by acceleration of reactivity (promotion of reactivity).

Therefore, it is possible to provide a higher-quality photomask blank as compared with a conventional photomask blank.

[Brief Description of the Drawings]

[Fig. 1]

It is a schematic diagram showing an internal constitution of an apparatus according to one example of the present invention.

[Description of Reference Numerals]

- 1: Vacuum chamber
- 2: Anode
- 3: Magnetron cathode
- 4: Backing plate
- 5: Target
- 6: Substrate
- 7: Sputtering gas introducing port
- 8: Exhaust vent
- 9: Sputtering DC power source
- 11: Ion source
- 12: Gas introducing port for ion source
- 13: Anode and cathode power source controller for
ion source

[Name of Document] Abstract

[Abstract]

[Object] It is an object of the present invention to provide a method of manufacturing a photomask blank that enables a reduction of a warp of a substrate caused by a film stress and an enhancement of density and denseness.

[Structure] In a method of manufacturing a photomask blank by forming an opaque film or a semi-transmission film on a transparent substrate, the opaque film or the semi-transmission film is formed by irradiating a film material being deposited onto the substrate 6 with ions generated by an ion generator (hereinafter, referred to as ion source 11) separately disposed in a film formation chamber during the deposition of the opaque film or the semi-transmission film on the substrate 6 by a sputtering method.

[Selected Figure] Fig. 1

[NAME OF DOCUMENT] DRAWING
[FIG. 1]

